IPST Technical Paper Series Number 552

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January 1995

Submitted to
Intern. Symp. Wood and Pulping Chemistry
June 6–9, 1995
Helsinki, Finland

CELLULOSE CHAIN CLEAVAGE REACTIONS UNDER PULPING CONDITIONS

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Abstract. The strength of paper is related to the cellulose polymer chain length. During pulping, undesirable chain cleavage reactions occur. The mechanisms of such reactions have typically been studied with models of cellulose, such as 1,5-anhydrocellobiitol. The chemistry observed is generally assumed to predict the reactivity of the cellulose. However, the reactivities and points of bond cleavages with disaccharide models may differ substantially from cellulose because of differences in molecular flexibility. We have studied a conformationally rigid cellulose model, the 4,6-O-benzylidene of 1,5-anhydrocellobiitol, under alkaline pulping conditions. Heating the model at 170°C in 2.5N NaOH gave 55% glycon-oxygen (G-O) bond cleavage, and ~45% oxygen-aglycon (O-A) bond cleavage. The amount of observed O-A bond cleavage is significantly higher than that for 1,5-anhydrocellobiitol, which is a more conformationally flexible cellulose model. The benzylidene model also degraded about ~35% faster than 1,5-anhydrocellobiitol; much of this rate increase can be attributed to a faster rate of O-A bond cleavage for the benzylidene. These results point out the value of choosing appropriate cellulose models and provide a better understanding of the mechanisms of cellulose chain cleavage reactions under pulping conditions.

Keywords. Cellulose Models, Chain Cleavage, Pulping

INTRODUCTION

The stringent conditions (170°C, 2.5 N NaOH) of chemical pulping lead to as much as a 10% loss in cellulose yield (1), together with a factor of three or more decrease in degree of polymerization of the cellulose (1-3). The latter results in lower pulp viscosities and, hence, lower pulp properties. The drastic reductions in the molecular weight are attributed to the random cleavage of the glycosidic bonds linking the glucose units of cellulose together (4).

Most of the mechanistic studies of alkaline cellulose chain cleavage chemistry have involved model compounds, rather than cellulose itself. Early models employed phenyl glycosides (**1**) and alkyl glycosides (**2**). The major proposed mechanism for glycosidic bond cleavage for these models is an $S_N$icB(2) mechanism (Figure 1) (5,6). The $S_N$icB(2) refers to a nucleophilic substitution by an internal nucleophile - the

conjugate base of the C2 hydroxyl group. The $S_N$icB(2) mechanism requires that the molecule flip from its more stable all-equatorial conformation to its all-axial conformation; this permits backside attack by the C2 oxyanion at C1, displacing the aglycon. Such a ring flip would be impossible for crystalline cellulose and probably difficult for amorphous cellulose polymer segments.

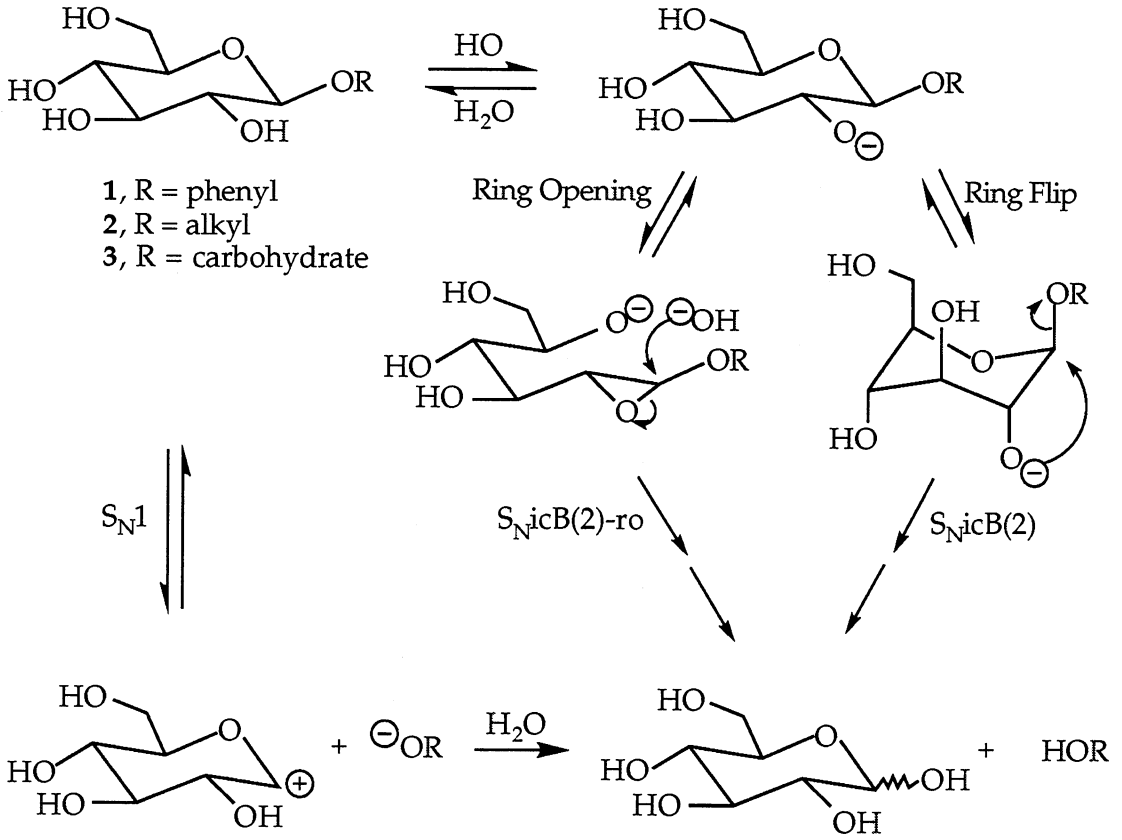

Figure 1. Mechanisms for Glycosyl-Oxygen (G-O) Bond Cleavage.

More recent studies have involved disaccharide models (**3**) and have shown that heating with alkali leads to a predominance (~90%) of glycosyl-oxygen (G-O) bond cleavage by way of a number of mechanisms, including S_N1, $S_N$icB(2), and $S_N$icB(2)-ro (7-9). The latter is a neighboring group mechanism that involves ring opening of the glycon as an intermediate step (Figure 1).

We have studied the alkaline degradation of a model compound that has less conformational mobility than previous models and, thus, presumably more similar to the rigid cellulose polymer chains found in wood and pulp. The new model is 1,5-anhydro-4-O-(4,6-O-benzylidene-β-D-glucopyranosyl)-D-glucitol (**4**). This nonreducing disaccharide will be referred to as benzylidene 1,5-anhydrocellobiitol.

EXPERIMENTAL

The detailed experimental conditions related to the preparation and characterization of the cellulose model **4**, as well as its degradation reactions in NaOH solutions, are described elsewhere (10). In general, the alkaline degradations were conducted in 4-mL stainless steel pressure vessels ("bombs"). The carbohydrate samples (0.03-0.04 mmoles per sample) were weighed into the bombs, and a NaOH solution (typically 250 equiv.) was added. The bombs were sealed and heated (with agitation) in a fluidized sand bath at 170°C. The bombs were removed at set time periods, cooled to room temperature, opened, and a gas chromatography (GC) internal standard added. The resulting mixture was neutralized with excess aqueous 5% ammonium chloride. An aliquot of the sample solution was concentrated in vacuo, silylated, and analyzed by GC.

RESULTS AND DISCUSSION

Products of the Degradation Reaction

Alkaline degradations of benzylidene 1,5-anhydrocellobiitol gave both alkali-stable and alkali-labile products (Figure 2). The alkali stable products from the nonreducing (aglycon) unit were identified by comparing GC retention times and GC/mass spectra to known compounds. The expected aglycon product, 1,5-anhydro-D-glucitol (**6**), was found in 55% ± 2% yield. A second aglycon product, 1,5:3,6-dianhydro-D-galactitol (**7**), was produced in 32% ± 5% yield. In addition, 0.5-2% of 1,5-anhydrocellobiitol (**8**) was formed, presumably by the degradation of the 4,6-O-benzylidene linkage. Compound **8** will break down to form additional 1,5-anhydro-D-glucitol (7); however, the rate is considerably slower than degradation of **4**. The 1,5-anhydro-D-glucitol coming from **8** represented only a small fraction of the overall source of 1,5-anhydro-D-glucitol and, thus, did not interfere with our study.

Some products could not be identified by GC/MS and were deduced to be polar, secondary degradation products of alkali-labile 4,6-O-benzylidene-D-glucopyranose (**9**). The latter, which contains a reducing end group, would be formed from either G-O or A-O bond cleavage and would quickly degrade by peeling-type reactions to smaller fragments under the reaction conditions. A sample of **9** was prepared and degraded under the same conditions (2.5 N NaOH, 170°C) to confirm this hypothesis. After heating for 5 hours, the solution containing **9** was worked up in the same way as **4**. The GC analysis showed that 26 signals from the degradation of the glucose benzylidene **9** had identical retention times to the "unidentified" signals found in the alkaline degradation of the model compound **4**.

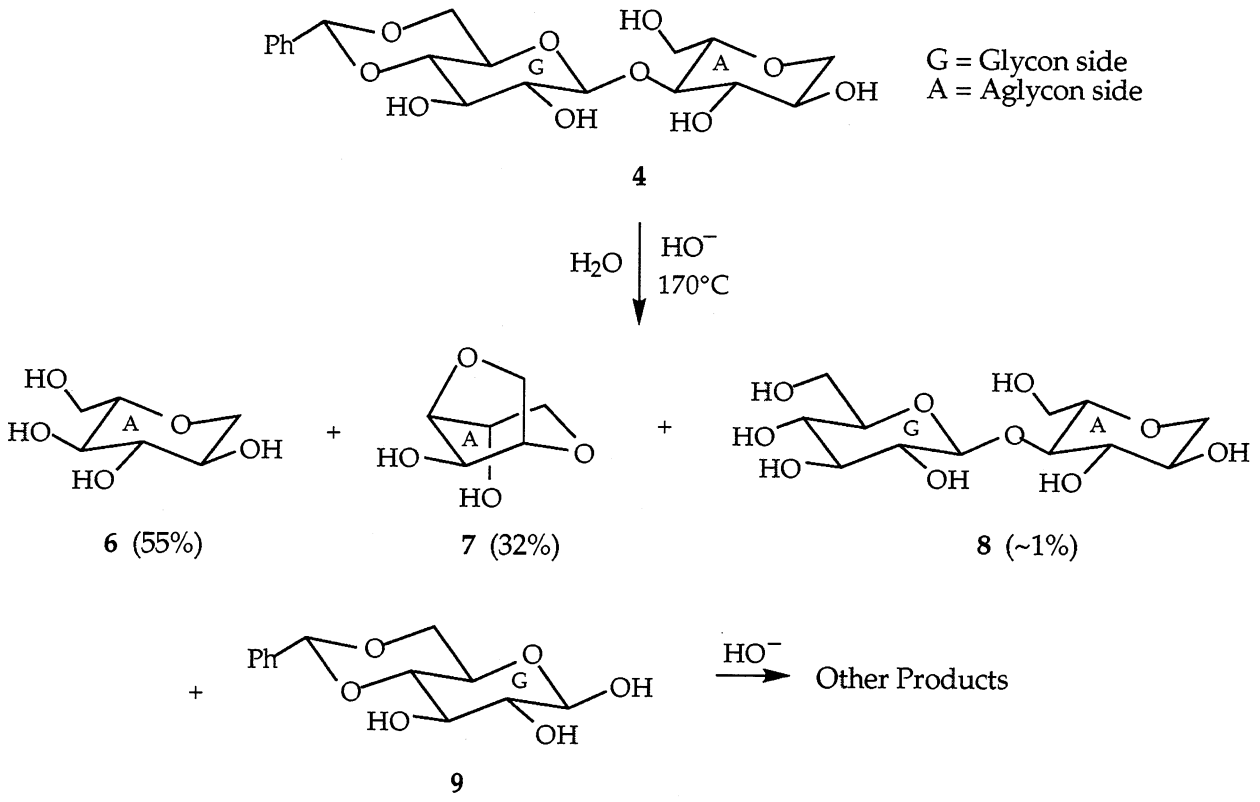

Figure 2. Alkaline Degradation Products from **4**.

A 170°C degradation of the model compound **4** in the presence of ^{18}O-enriched aqueous sodium hydroxide (2.5 N NaOH) led to no ^{18}O enrichment in either the two main products, 1,5-anhydro-D-glucitol and 1,5:3,6-dianhydro-D-galactitol. Thus, all of the 1,5-anhydro-D-glucitol was formed by G-O bond cleavage.

Kinetic Analysis of the Degradation Reaction

The disaccharide model **4** was heated at 170°C in aqueous sodium hydroxide and samples taken from 2 to 98 hours; the rate of disappearance of the model compound and the rate of appearance of its degradation products were followed. Pseudo-first-order kinetics (7) were assumed since a 250-fold excess of hydroxide ion was used at constant ionic strength. Several replicate degradations were done for model **4** and for 1,5-anhydrocellobiitol (**8**). The observed degradation rates ranged from 10.0-11.4 x 10^{-6} sec^{-1} for the benzylidene **4**, and 7.2-8.7 x 10^{-6} sec^{-1} for compound **8**. Previous investigators observed a rate constant of 7.9 x 10^{-6} sec^{-1} for compound **8**, which is exactly in the middle of our range. If we use this value for **8** and our average value for **4** (10.7 x 10^{-6} sec^{-1}), we come to the conclusion that the benzylidene 1,5-anhydrocellobiitol degrades ~35% faster than 1,5-anhydrocellobiitol.

The rate of degradation of **4** was also determined at a lower NaOH concentration. The hydroxide concentration was decreased by 75% (to 0.62 N) while, at the same time, the ionic strength of the reaction medium was kept constant (2.5 N) by adding a NaCl. The results of this experiment showed a 30% decrease in the degradation rate; namely, the overall rate was 7.0 ($\pm$ 0.1) x 10^{-6} sec^{-1}. The product distribution also changed at the lower NaOH level. The mole fractions and calculated rate constants for glycosyl-oxygen (G-O) bond and oxygen-aglycon (O-A) bond cleavage are shown in Table 1. The latter were obtained by multiplying the mole fractions by the overall rate constant.

Table 1. Product Mole Fractions and Rate Constants for the 170°C Alkaline Degradation of Benzylidene (**4**) and 1,5-Anhydrocellobiitol (**8**).

	Conc. (N)		Mole Fractions		Rate Constants (x10^6)	
Substrate	NaOH	NaCl	**6**	**7**	k_{G-O}	k_{O-A}
4	2.5	0	0.55	0.31	5.6	3.1
4	0.6	1.9	0.47	0.29	3.3	2.0
8[a,b]	2.5	0	0.92	0.10	7.3	0.9

[a]Data from Brandon et. al. (7).
[b]Blythe and Schroeder observed mole fractions of 0.88 and 0.10 for **6** and **7**, respectively, for reacting **8** at 170°C in 1.0N NaOH (11).

CONCLUSIONS

Upon heating with NaOH, the benzylidene 1,5-anhydrocellobiitol fragments by 55% glycosyl-oxygen (G-O) bond and ~45% oxygen-aglycon (O-A) bond. The former is the % 1,5-anhydro-D-glucitol formed; the latter is the % 1,5:3,6-dianhydro-D-galactitol (32%) and the undetermined products (13%). [The undetermined products were most likely O-A cleavage products since G-O cleavage always produces the detectable, stable 1,5-anhydro-D-glucitol.] The observed O-A bond cleavage amount was much higher than has been observed (~10%) with other cellulose models.

Since our model cannot flip to provide for a 1,2-diaxial elimination, we believe that the results of this study are best explained by an $S_N$icB(2)-ro mechanism for the G-O bond cleavage. The neighboring-group $S_N$icB(3) mechanism was concluded to be the most feasible mechanism for the A-O bond cleavage. However, the possible existence of a parallel, less dominant S_N1 mechanism cannot be ruled out for either

O-G or A-O cleavages. The rates of G-O and O-A bond cleavages were reduced when the concentration of the nucleophile was reduced, suggesting a mechanism other than S_N1 is involved in the cleavages.

The rate of degradation of benzylidene 1,5-anhydrocellobiitol (**4**) was 35% faster than of 1,5-anhydrocellobiitol (**8**) under identical conditions. The rate difference can be attributed to a much faster rate of O-A bond cleavage for the benzylidene. The rate of O-A bond cleavage was 350% faster for the benzylidene, while the rate of G-O bond cleavage was 30% slower for the benzylidene (Table 1). The increase O-A cleavage rate could be because the benzylidene-substituted glucoside is a better leaving group than an unsubstituted glucoside. The benzylidene, with less OH groups, will be less charged in alkali. A buildup of negative charges hinders the glucoside from leaving with the new negative charge. The fact that G-O bond cleavage is 30% faster in the unsubstituted 1,5-anhydrocellobiitol may indicate that both $S_N$icB(2) and $S_N$icB(2)-ro mechanisms are operating in this case, while only the ring opening mechanism operates in the benzylidene case.

Our data suggest that the ring opening mechanism could be the dominant G-O bond cleavage mechanism for both 1,5-anhydrocellobiitol models. Since pyranose ring flips should be difficult for carbohydrate polymers, random chain cleavage reactions of cellulose may also be occurring largely by an $S_N$icB(2)-ro mechanism.

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